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QUANTITATIVE TLC ANALYSIS OF AMINE ANTIOXIDANTS IN HIGH-TEMPERA--ETC(U)
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Quantitative TLC Analysis of Amine Antioxidants in High-Temperature Jet Engine Lubricants

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A quantitative (TLC) method with a relative standard deviation of four percent is described for the analysis of commonly used amine antioxidants in high-temperature jet engine lubricants. The method is convenient in that after development of the plates, the components develop characteristic visible colors suitable for analysis.

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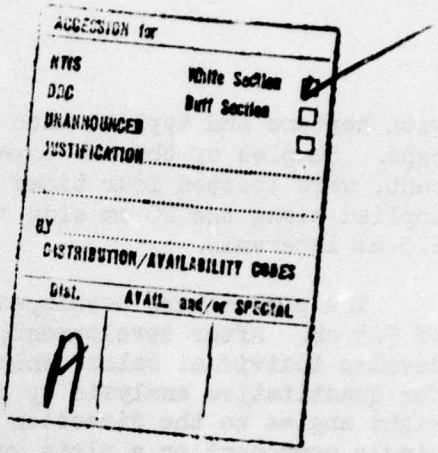

QUANTITATIVE TLC ANALYSIS OF AMINE ANTIOXIDANTS IN HIGH-TEMPERATURE JET ENGINE LUBRICANTS

INTRODUCTION

Secondary aromatic amines are commonly used antioxidant additives in both U. S. and British aircraft gas turbine engine lubricants (1,2). Three currently employed in many formulations are:

(I.) phenyl-alpha-naphthylamine,

(II.) p,p'-dioctyldiphenylamine, and

(III.) N-p-octylphenyl-alpha-naphthylamine,

where C-13 NMR analysis revealed the octyl structures for (II) and (III) to be 2,2,4,4-tetramethylbutyl.

This present report describes a quantitative TLC method of analyzing these components in aircraft gas turbine engine lubricants whose base stock is composed of various neopentylpolyol esters. The method was developed in the course of a study of additive behavior under engine operating conditions.

EXPERIMENTAL

A Kontes Densitometer K-49-500 (3) connected to a one-millivolt recorder and interfaced to a Perkin-Elmer PEP-1 data processor was used for evaluation of the chromatograms. Separation of the components was carried out on 10 x 20 cm E. Merck thin layer chromatography plates precoated with silica gel 60 F-254, with a layer thickness of 0.25 mm. Before use, the plates were developed in acetone and allowed to air-dry for one hour.

Standard samples of 1.0, 0.7, 0.5, 0.3, 0.1, 0.05, 0.025, and 0.01 percent of each of the additives were prepared in a base stock of suitable pentaerythritol esters. The oil samples were diluted 3 to 1

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with heptane and applied with 1-microliter Drummond disposable microcaps. Samples of the two lower concentrations, 0.025, and 0.01 percent, were spotted four times for suitable analysis. Spots were applied along the 20 cm side of the plate 1.5 cm from the edge at 2.5 cm intervals.

The plates were developed in heptane-toluene (50-50) to a height of 7.5 cm. After development, the separated components begin to develop individual colors which after 16 hours were sufficiently dense for quantitative analysis by densitometry. Spots were scanned at right angles to the direction of development so that all spots of a single component on a plate were analyzed during the same scan. Plates were scanned at 2 cm per min. with the reference head; the mode was single beam with long UV visible transmission. Both peak heights and areas were tabulated. Actual jet engine oils were treated the same as the calibration samples. Whether multiple spotting is necessary for the unknowns is determined by examination under long wave UV, where one spot of 0.025 percent concentration is barely visible.

RESULTS AND DISCUSSION

R_f values and the additive colors that formed were 0.59 and yellow for (I), 0.75 and yellow-orange for (II), and 0.84 and orange for (III). The formation of visible color is an autooxidative process since it does not occur if the plates are stored in an atmosphere of nitrogen. The oil basestock produces a colorless elongated spot with an R_f of 0.05. Figure 1 shows a recorder chromatogram of additive (II) from a plate containing a single one-microliter spot of each of the calibration samples. Multiple spotting (4X) is used with the two lower concentrations to improve precision. Analysis by data processor measurement of peak areas offered no improvement over measurement of peak heights; the calibration curves in Figure 2 are based on peak height measurements. In the construction of the curves, peak heights of the multiply-spotted samples were appropriately divided by 4. Curves for the three additives are seen to be nonlinear with the slope decreasing with higher concentrations. For best results calibration samples should be run at the same time as the unknowns, but not necessarily on the same plates. Analysis can be successfully carried out 16 hours after plate development. The colors reach a maximum in about two days and then gradually fade, amounting to a 10 percent decrease in densitometer signal after 20 days. The analytical results are not affected. Precision of the method as determined from peak height measurements of duplicate spots of the calibration samples was 3.6 percent in terms of the relative standard deviation.

As indicated earlier, the samples of most interest are oils that have seen use in aircraft engines or in suitable testing devices. As the additives are depleted during use, components form that have characteristic R_f values. If the three additives were all present in a formulation, the interference of these components with the original

additives in the analysis would be of some concern. However, this situation has never been experienced in the examination of numerous formulations.

As an example of how the analytical data were used, results from oxidation bench tests of oils containing additives (I) and (II) gave a calculated relative reactivity [ln fract. of (I) remaining/ln fract. of (II) remaining] of about 2. The first set of entries in Table 1 is typical of such a test. However, the second set of entries from an oil after aircraft engine use gave quite a different result, a relative reactivity of about 8. This suggests that the particular bench test employed was not entirely appropriate in simulating additive depletion in the engine.

TABLE I

Depletion of Additives (I) and (II) in Oxidized Oils

Test Hrs.	Percent (I)	Percent (II)	$\frac{\ln \text{ fract. (I) remain.}}{\ln \text{ fract. (II) remain.}}$
		Bench Test Results	
0	1.00	1.00	-
25	0.24	0.52	2.2
50	0.11	0.30	1.8
75	0.051	0.23	2.0
		Aircraft Engine Test	
0	0.72	0.94	-
54	0.36	0.86	7.8
120	0.24	0.82	8.0

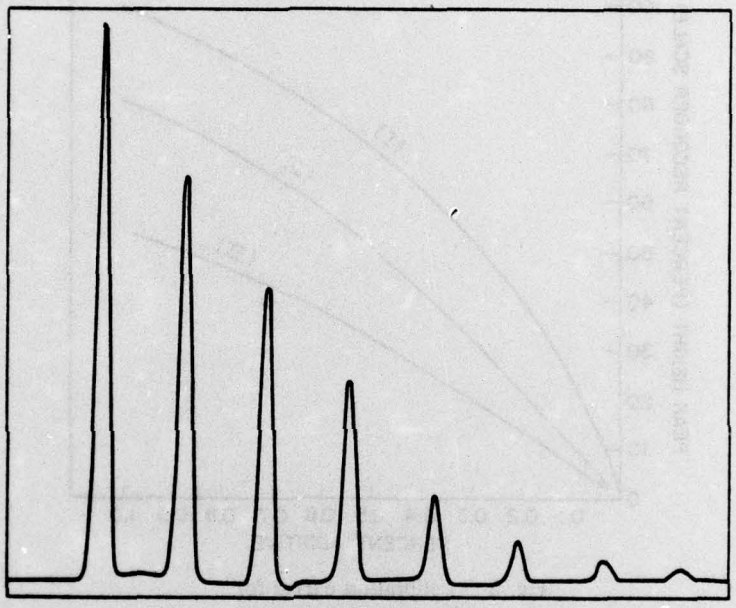

Fig. 1 — Recorder output for scan of developed TLC plate from single 1-microliter spots of the calibration standards diluted 3-to-1 with heptane: 1.0, 0.7, 0.5, 0.3, 0.1, 0.05, 0.025, and 0.01 percent of additive (II).

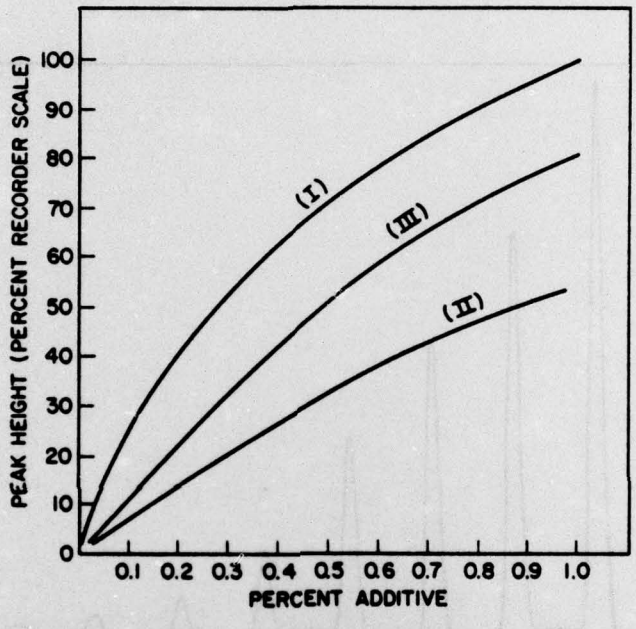

Fig. 2 — Calibration curves for amine antioxidants.

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